INFLUENCE OF THE PREPARATION MODE ON STRUCTURE AND PROPERTIES OF GELS BASED ON POLY(ACRYLAMIDE)

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Introduction

Copolymers of acrylamide (AA) and N,N'-methylene-bis-acrylamide (MBAA), obtained by the ion-radical copolymerization in the presence of ammonium persulfate in the mid 70th, has been used in medical applications as the depot for medicine drugs and the immobilizing matrix for albumen [1]. After that, the water-swelling polymers has been used in the plastic surgery as the implants for the face plastic and the plastics of soft tissues [2-8]. The advantage of this copolymer compared with the other injection materials is in the fact that the content of the copolymer in the water gel is just 3-4 %. Because of this, the gel amount incorporated into the organism can be 200-300 g. For the other injection polymer materials, the incorporation of more than 2-3 g. can cause a painful shock.

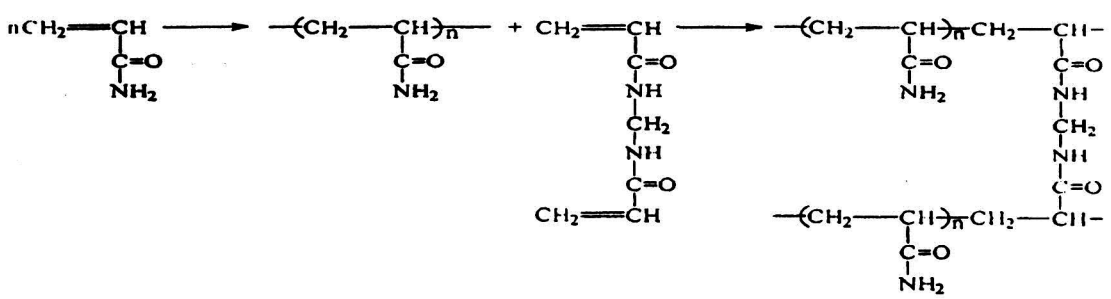
In the works [9-10], there are the results of the study of the effect of the synthesis conditions and the copolymer content in the gel on the swelling and the network structure. The authors of the works used the classical theory of Flory-Rainer. The works gave an assumption of the structure and properties of such kind of polymers, and also the behavior of gels based on them. However, the effect of copolymers structures, obtained in different conditions, including the conditions of different actions on the gels, and the histology action on the albumen tissue, has not been studied yet in details.

In this work, we have investigated the effect of conditions of the gels based on the mentioned copolymers preparation on their structure, and its effect on the organism reaction on the tissue.

Experimental Part

Four samples of the water-swelling copolymer of AA with MBAA in the ratio of 1: 0.1 - 0.08, correspondingly, were investigated. The copolymers were prepared by the radical copolymerization in the presence of ammonium persulfate. The dry residue was 3.5 - 4.5 %.

The sample 20/1 was obtained on the first stage of the process, in which the copolymerization of AA and MBAA occurs in the aqueous media at temperature up to 90°C. The process most probably occurs according to the following scheme:

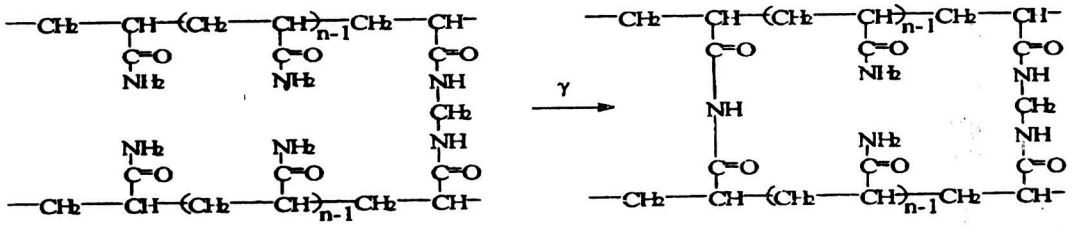


The sample 20/1, at histological investigation gives aseptic tissue inflammation, and the cause of such effect

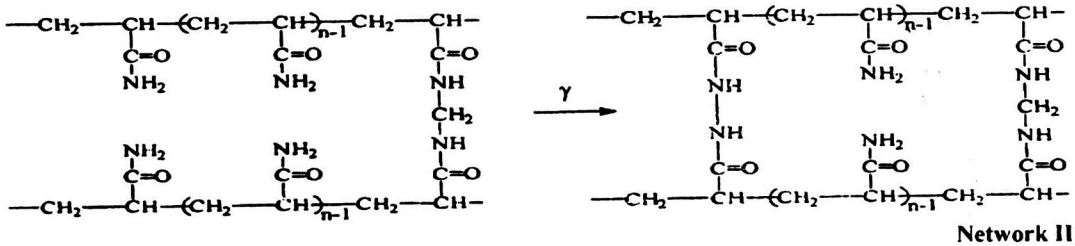
is not known yet.

The sample 20/2 is obtained on the process second stage by γ-irradiation according to the following scheme [11-12].

Thus, based on the literature data, which are only an assumption, at γ-irradiation two types of polymer network can be formed. The network differ in the chemical structure



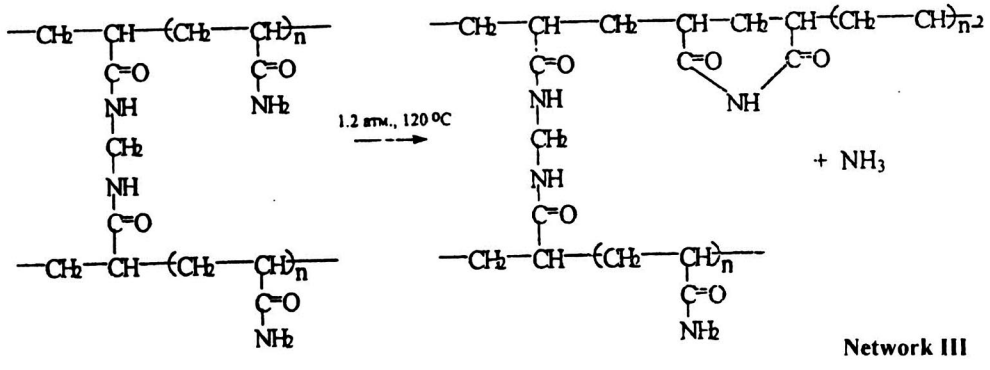
Network I



Network II

At studying the histology of sample 20/2, we have established that the gel does not cause the aseptic inflammation, the tissue reaction is very weakly expressed. After two months, around the gel, a thin connecting tissue capsule is formed. This capsule does not transform into the fibrous one, what is happening usually at usage of other polymers.

The sample 20/3 was formed after sterilization of the initial copolymer at 120°C and the pressure of 1.2 atm for 40 min. In this case, the gel pH shifts towards the alkali media from pH=3.5-4.0 till pH=5-8 depending on the treatment duration. During the process in the autoclave, the ammonia smell is noticed, the gel becomes less dense (diluted). It is possible that during the autoclave treatment, the following processes take place:



Network III

At conducting the tests on animals, this gel quickly swelled and disintegrated.

The sample 20/4 was obtained by the second γ-irradiation. In this case, the gel becomes more dense and poorly swells in the water media. At testing the gel on animals, the gel gives very good tissue reaction.

It follows from the data discussed above that on the different stages of the process, the gels formed with the structures having different tissue reaction. However, the reason of such influence is not clear, and the all explanations have the character of assumptions. Because of this, in this work, we have conducted an analysis of the chemical transformations of the gels based on the copolymer of AA and MBAA. The analysis was conducted by various methods.

First of all, it was conducted the thermo-mechanical investigations of the all four samples of the dry polyacrylamide and its copolymers with N.N'-methylene-bis-acrylamide. The measurements were conducted on carefully dried samples to provide the copolymer concentration in the samples was close to 100%. The thermo-mechanical curves were obtained in conditions of indenter (dia. 4.0 mm) penetration under the load on it equal to 100 g. The thermo-mechanical curves for all four samples are shown on Fig.1.

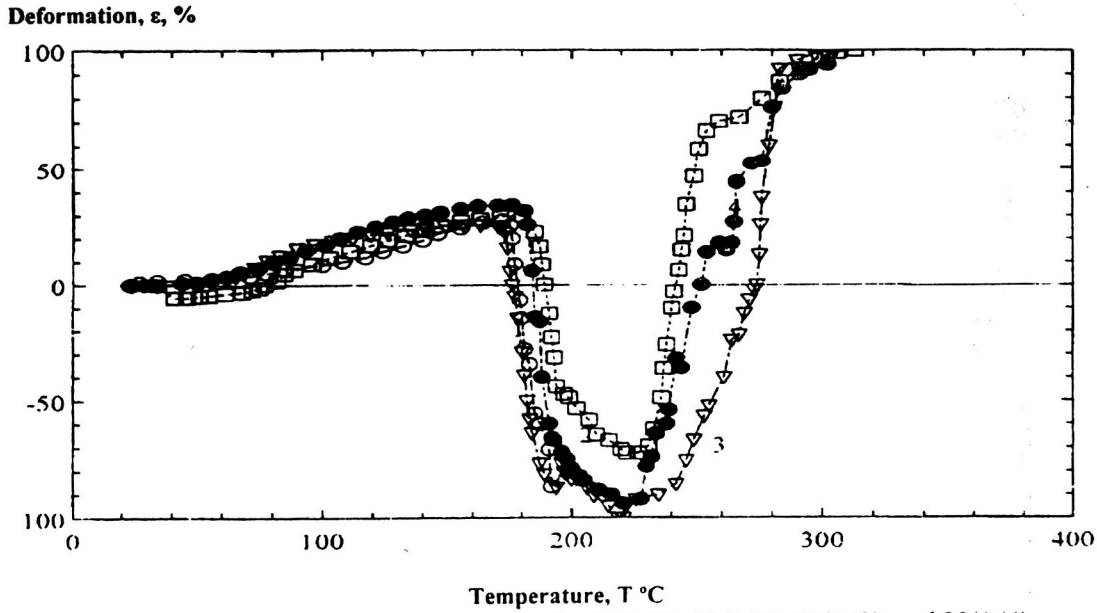


Figure 1. The thermo-mechanical curves for samples 20/1 (1), 20/2 (2), 20/3 (3), and 20/4 (4).

It is seen that at heating, the samples begin to soften at temperature around 100°C, but at temperature close to 170°C, there is a clear appearance of the 'negative' deformation, which witnesses the quick increase of the samples volume. Such character of the thermo-mechanical behavior of polymers was analyzed in details in the works [13-15]. The behavior is connected with the fact that at drying of polyacrylamide gels, high internal stresses are created. The stresses are eliminated at the glass transition temperature, and the sample is rapidly expanded. After the stresses elimination, the deformation of samples is quickly increased and reaches 100% at 280-300°C. It should be also taken into account the circumstance that the networks based on polyacrylamide absorb quickly the air moisture, what can also distort the character of the thermo-mechanical curves.

To find out the reasons of the properties change of the gels based on polyacrylamide and N,N'-methyl-bis-acrylamide at γ-irradiation, the following calculations were performed. In the first place, the physical characteristics of polyacrylamide were calculated. The calculation was performed by using the program CHEOPS developed by MiilionZillion Software Company (USA). The basis of the program is the quantitative analysis of the effect of the chemical structure of the linear and networked polymers, described in the works [14, 15]. The results of the calculations are given in Table 1. Whenever it is possible, the experimental values of some characteristics are given in the brackets.

Let us discuss the effect of certain polymeric chemical structure on their properties. The polymer density is significantly increasing at changing from polyacrylamide to the network system based on MBAA and further to the networks I and II. The glass transition temperature is, naturally, sharply increases at transition from linear polyacrylamide to the MBAA networks and to the networks I and II. On the contrary, the temperature of the intense thermal destruction start is changing insignificantly, however the temperature is significantly lower than the glass transition temperature, which, hence, cannot be measured experimentally for these networks due to their destruction at much lower temperature. Such experimental evaluation can be done only based on the analysis of the glass transition temperature dependence on the copolymer composition. The

copolymers should be synthesized and tested. The procedure of such analysis is described in [16].

Table 1. Properties of polyacrylamide and the networks based on it.

Polymer	Polymer properties*					
	MM	V_m, cm^3/mol	$\sum_i \Delta V_i$, Å^3	ρ, g/cm^3	T_g, K	T_d, K
Polyacrylamide	71.1	56.8	64.3	1.25	421 421-441 (exper.)	569
Network based on N,N'-methylene-bis-acrylamide	154	119	134	1.30	677	562
Network I	125	93.2	105	1.34	913	589
Network II	140	104	104	1.35	828	551

Polymer	Polymer properties*						
	γ, dyne/cm	E*, kJ/mol	α_h, rel. units	α_{dd}, rel. units	α_d, rel. units	ε, rel.units	E, kJ/mol
Polyacrylamide	50.7	54.0	0.447	0.185	0.368	4.95	76.9
Network based on N,N'-methylene-bis-acrylamide	49.9	111.0	0.433	0.179	0.388	4.93	260
Network I	54.7	73.6	0.328	0.271	0.401	4.40	267
Network II	55.3	107.0	0.449	0.186	0.365	5.70	272

Polymer	Polymer properties*					
	E_{dd+h}, kJ/mol	E_d, kJ/mol	δ, $(J/cm^3)^{1/2}$	n, rel. units	ΔU, kJ/mol	$\alpha_G \cdot 10^{-4}$, K^{-1}
Polyacrylamide	44.6	32.3	30.8	1.52	91	2.28
Network based on N,N'-methylene-bis-acrylamide	177	83.3	30.6	1.54	146	1.42
Network I	196	70.6	28.1	1.54	197	1.05
Network II	204	68.8	32.1	1.56	179	1.16

Polymer	Polymer properties*					
	$\alpha_l \cdot 10^{-4}$, K^{-1}	n_e, rel. units	C_p^S, J/mol·Deg	C_p^S, J/mol·Deg	R, cm^3/mol	M_e
Polyacrylamide	5.73	299	98.2	191	17.3	21200
Network based on N,N'-methylene-bis-acrylamide	3.56	-	197	329	37.4	-
Network I	2.64	-	152	240	29.1	-
Network II	2.91	-	174	327	33.6	-

Polymer	Polymer properties*					
	P, cm^3/mol	C_σ, B	μ, D	P_{O2}, DU	P_{CO2}, DU	P_{N2}, DU
Polyacrylamide	32.3	101	0.853	$1.84 \cdot 10^{-5}$	$2.02 \cdot 10^{-5}$	$1.32 \cdot 10^{-6}$
Network based on N,N'-methylene-bis-acrylamide	67.4	86.4	1.21	$2.31 \cdot 10^{-5}$	$2.59 \cdot 10^{-5}$	$1.69 \cdot 10^{-6}$
Network I	49.5	49.2	0.994	$31.6 \cdot 10^{-5}$	$44.8 \cdot 10^{-5}$	$2.86 \cdot 10^{-5}$
Network II	63.6	92.4	1.21	$2.2 \cdot 10^{-6}$	$2.0 \cdot 10^{-6}$	$1.33 \cdot 10^{-7}$

Notes: MM is the molecular mass of the repeating chain fraction; V_m is the molar volume; $\sum_i \Delta V_i$, is the Van-der-Waals volume; ρ is the density; T_g is the glass transition temperature; T_d is the onset temperature of the thermal degradation; γ is the surface energy; E^* is the cohesive energy; α_h is the ratio of the hydrogen bonds energy to the total cohesive energy; α_{dd} is the ratio of the dipole-dipole interaction energy to the total cohesive energy; α_d is the ratio of the dispersion interaction energy to the total cohesive energy; ε is the dielectric constant; E is the total energy of the intermolecular interaction; E_{dd+h} is the energy of the dipole-dipole interaction and the hydrogen bonds; E_d is the energy of the dispersion interaction; δ is the solubility parameter; n is the refractive index; ΔU is the activation energy of the low-temperature γ-transition; α_G is the coefficient of the thermal expansion in the glassy state; α_L is the coefficient of the thermal expansion in the rubbery state; n_e is the polymer degree of polymerization, when the rubbery state appears; C_p^S is the molar heat capacity in the glassy state; C_p^l is the molar heat capacity in the rubbery state; R is the molar refraction; M_e is the molecular mass of polymer, when the rubbery state appears; P is the polarizability; C_σ is the stress-optical coefficient; μ is the dipole moment; P_{O2}, P_{CO2}, P_{N2} are the permeabilities by oxygen, carbon dioxide, and nitrogen, respectively (the unit of permeability measurements is 1 DU= $0.45 \cdot 10^{-10}$ $cm^2 \cdot s^{-1} \cdot atm^{-1}$).

The surface energy is weakly dependent on the given polymers structure, but the molar energy of cohesion, naturally, increases at transition from polyacrylamide to the networked systems. This is due to the fact that molar volume of the repeating fragment is significantly rising. In respect to the specific energy of cohesion (the Hildebrand's solubility parameter), it should be noted that its value is approximately the same at transition from polyacrylamide to the network based on MBAA. The value reduces at transition to the network I, but it increases at transition to the network II. It is very important at evaluating of the interaction of polymer with solvent, in particular, with water.

The fraction of the hydrogen bonds energy, the energy of the dipole-dipole interaction, and the fraction of the dispersion interaction energy of the total cohesion energy is closely the same for polyacrylamide, for the network based on MBAA, and the network II. However, the fraction of the hydrogen bonds energy and the energy of the dipole-dipole interaction is significantly lower for the network I, and the fraction of the energy of the dispersion interaction is significantly higher. Thus, polyacrylamide and the networks based on MBAA, and also the network II have significantly higher specific intermolecular interaction compared with the network I, and, hence, they have higher affinity toward water, which has a very high fraction of the hydrogen bonds energy.

The dielectric constant of polyacrylamide and the network based on MBAA is closely the same, but it significantly reduces for network I and increases for the network II. The refractive index is approximately the same for all four polymers. The effective dipole moment increases at transition from polyacrylamide to the network based on MBAA and to the network II, but it is lower for network I compared with the network II.

It is seen from the data in Table 1 that the calculated value of the glass transition temperature, T_g of polyacrylamide is 421 K. The experimental values of T_g based on the literature data is in the interval 421 - 436 K. the temperature of the sharp deformation change according to the thermo-mechanical measurements (Fig.1) is ~443 K, what corresponds to the glass transition temperature.

Among the other properties, which are important for the practical application of polyacrylamide, we should mention the large portion of the energy of the dipole-dipole interaction and the energy of hydrogen bonds from the total energy of the intermolecular interaction (0.579), and also a large portion of the hydrogen bonds from the total cohesion energy (0.447). The solubility parameter of polyacrylamide is 30.8 J/cm^3, and the surface energy is 50.7 dyne/cm.

The properties of the networked samples based on copolymers of AA and MBAA were also calculated. Due to the fact that the concentration of MBAA is very small (less than 1%), the properties of such copolymer are very close to the ones of polyacrylamide. Further, by using the calculating program, the properties of the polymer networks I and II at different crosslink density were calculated.

The calculations were performed according to the formula (1) [14-15] shown below. After incorporation of the numeric values of all parameters into equation (1). we obtained the expressions for the dependence of the glass transition temperature, T_g on the molar fraction, α, of the networks or the cyclic structure (equations (2)-(4).

$$T_g = \frac{\alpha_1\left(\sum_i \Delta V_i\right)_1 + \alpha_2\left(\sum_i \Delta V_i\right)_2 + \ldots + \rightarrow}{\alpha_1 \frac{\left(\sum_i \Delta V_i\right)_1}{T_{g,1}} + \alpha_2 \frac{\left(\sum_i \Delta V_i\right)_2}{T_{g,2}} + \ldots + \alpha_n \frac{\left(\sum_i \Delta V_i\right)_n}{T_{g,n}} + \rightarrow} \quad (1)$$

$$\rightarrow \frac{+ \alpha_n\left(\sum_i \Delta V_i\right)_n}{+ [\alpha_1(1-\alpha_1) + \alpha_2(1-\alpha_2) + \ldots + \alpha_n(1-\alpha_n)] \cdot 0.03},$$

where: T_{g1}, T_{g2}, ... T_{gn} are the glass transition temperatures of polymers obtained from components 1,2,...n; $(\sum\Delta V_i)_1$, $(\sum\Delta V_i)_2$ ... $(\sum\Delta V_i)_n$ are the Van-der-Waals volumes of the repeating fragments of the homopolymer chains obtained from the components 1,2...n; α_1, α_2, ...α_n are the molar portions of components 1,2,...n.

For network I

$$T_g(K) = \frac{64.3 + 40.7\alpha}{0.1527 + 0.0223\alpha - 0.06\alpha^2} \quad (2)$$

For network II

$$T_g(K) = \frac{64.3 + 39.7\alpha}{0.1527 + 0.0329\alpha - 0.06\alpha^2} \quad (3)$$

For the cyclic structure III

$$T_g(K) = \frac{64.3 + 40.7\alpha}{0.1527 + 0.0394\alpha - 0.06\alpha^2} \quad (4)$$

Fig.2 shows the glass transition temperature dependence on the composition of networked polymer, formed according to the schemes I and II.

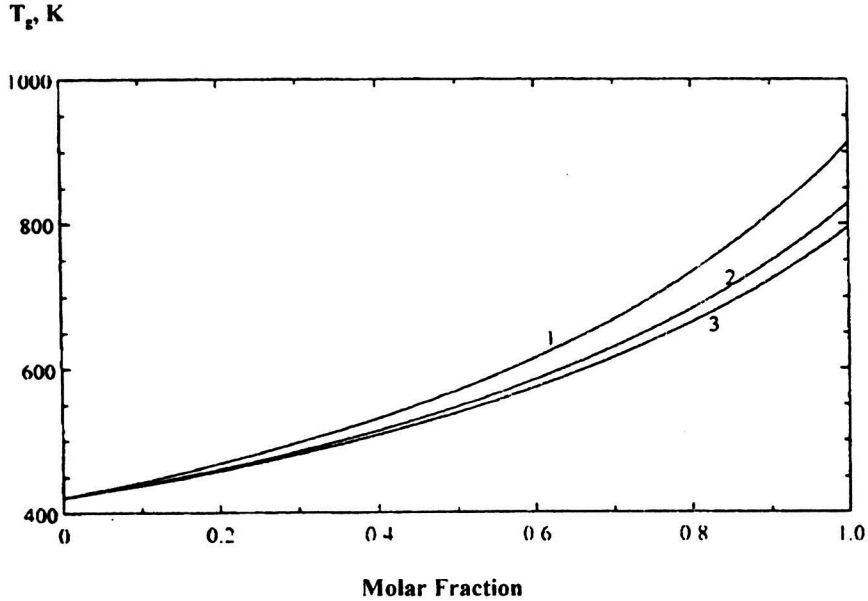


Figure 2. Glass transition temperature, T_g dependencies on the molar fraction of networks I (1), II (2), and the cyclic structure III (3).

It is clearly seen that in case of the crosslink density would significantly increase at γ-irradiation, the glass

transition, T_g of such networked system could be sharply increased. However, based on the experimental data, the increase of T_g is relatively small, and it is found only for samples 20/2 and 20/4. Thus, if the crosslinking at γ-irradiation takes place, it is only in a very small state.

After that, the dependence of the glass transition temperature of the networks, containing different amount of the assumed cyclic structure III, were calculated. The results of calculation in the form of the T_g dependence on the cyclic structure III content are given in Fig.2. It is seen that in case the cyclic structure III amount would have been in an appreciable amount, the glass transition temperature of such system would sharply rise. However, based on the experimental data (Fig.1), the characteristic practically did not change in the course of the initial copolymer sterilization at 120°C and pressure 1.2 atm. for 40 min.

Conclusions

The results of experiments and calculations show that at γ-irradiation of copolymers of acrylamide and N.N'-methylene-bis-acrylamide, the formation of additional crosslinking is possible, but only in a small amount (several percentage points). However, even so small amount of crosslinking leads to a clearly expressed effect on the tissue reaction. The results of fine analysis of the chemical transformation at the γ-irradiation will be presented in our next paper.

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